

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problems Mailbox.**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification<sup>5</sup> :</b> <b>B05D 5/12, 3/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 91/16149</b> <b>(43) International Publication Date:</b> 31 October 1991 (31.10.91)
<b>(21) International Application Number:</b> PCT/US91/01791 <b>(22) International Filing Date:</b> 18 March 1991 (18.03.91) <b>(30) Priority data:</b> 510,115 17 April 1990 (17.04.90) US <b>(71) Applicant:</b> MASSACHUSETTS INSTITUTE OF TECHNOLOGY [US/US]; 77 Massachusetts Avenue, Cambridge, MA 02139 (US). <b>(72) Inventors:</b> CIMA, Michael, J. ; 28 Burlington Road, Lexington, MA 02173 (US). MCINTYRE, Paul ; 209-B, 305 Memorial Drive, Cambridge, MA 02139 (US).		<b>(74) Agent:</b> PASTERNAK, Sam; Choate, Hall & Stewart, Exchange Place, 53 State Street, Boston, MA 02109 (US). <b>(81) Designated States:</b> AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PREPARATION OF HIGHLY TEXTURED OXIDE SUPERCONDUCTOR FILMS FROM PRECURSOR SOLUTIONS  <b>(57) Abstract</b> <p>Highly-textured superconductor oxide thin films are prepared on substrates, including lattice matched, non-lattice matched, inert and non-inert materials, by metal organic deposition (MOD). Precursor solution composition, as well as processing temperature and atmosphere are selected to control the presence of a transient liquid phase. Superconductor oxide films characterized by highly textured morphologies and fully dense, homogeneous microstructures are capable of sustaining critical current densities in excess of <math>10^4</math> A/cm<sup>2</sup> at 77 K when prepared on non-lattice matched substrates or critical current densities in excess of <math>10^6</math> A/cm<sup>2</sup> at 77 K when prepared on lattice-matched substrates.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

PREPARATION OF HIGHLY TEXTURED OXIDE  
SUPERCONDUCTOR FILMS FROM PRECURSOR SOLUTIONS

BACKGROUND OF THE INVENTION

The invention relates to fabrication of thin film oxide superconductors.

Metal organic deposition (MOD) is a method for fabrication of uniform thickness thin films from liquid precursor solutions as described by Y.L. Chen et al., J. Mater. Res., 4, 1065 (1989). Commonly, metal carboxylates dissolved in organic solvents are deposited on polished substrates by dipping or spin coating with a photoresist spinner. The green precursor films produced by this coating process are transformed into superconductor films by selective heat treatment which often involves multiple distinct calcination steps. Metal organic deposition techniques can be used to deposit films of uniform and controlled composition rapidly and without a need for sophisticated vacuum systems, J.V. Mantese et al., MRS Bull., 14, 48 (1989).

Several investigators have reported preparation of  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  (BYC) thin films using metal organic deposition including, Y-M. Chiang et al., Mat. Res. Soc. Symp. Proc., 22, 307 (1988); M.E. Gross et al., Appl. Phys. Lett., 52, 160 (1988); T. Kumagai et al., Chem. Lett., 1645 (1987); M. Klee et al., J. Crys. Growth, 91, 346, (1988). However, these workers observe that the electrical transport properties of metal organic deposited BYC films prepared from metal carboxylate precursors are generally inferior to sputtered, coevaporated and laser ablated films such as those prepared by R.L. Burton et al., submitted to SERI conference, Colorado Springs, CO, November, 1988; S-W. Chan et al., J. Appl. Phys., 65, 4720 (1989); and P.M. Mankiewich et al., Appl. Phys. Lett., 51, 1753 (1987). Residual precursor materials trapped in MOD films may be responsible for these inferior properties; however,

the high processing temperatures needed to completely eliminate precursor residues can cause undesirable reactions between the superconductor film and substrate.

#### SUMMARY OF THE INVENTION

According to the invention, a superconducting oxide thin film is fabricated by preparing a precursor solution containing film cation constituents in a stoichiometry nearly equal to that of the final oxide film product. The phrase "nearly equal" denotes a stoichiometry deviation from that of the final superconducting oxide film which can occur when constituents volatilize during processing. A coating of the precursor solution is applied to a substrate and exposed to a heat treatment and atmosphere selected to control the presence of a transient liquid phase during the firing process which yields the superconducting oxide film.

In preferred embodiments, the precursor solution may contain organic compounds such as metal trifluoroacetates and methyl alcohol. The precursor solution can be applied to the substrate by spinning, spraying, or painting or by dipping the substrate in the precursor solution. Superconductor oxide films can be fabricated on substrates having varied geometry including flat and three dimensional substrates including ribbon, wire or coil geometries. Substrates can be single crystals lattice matched to the final superconductor such as (001)  $\text{SrTiO}_3$ , (001)  $\text{LaAlO}_3$ , (001)  $\text{LaGaO}_3$  and (001)  $\text{NdGaO}_3$  or can be non-lattice matched compounds such as  $\text{BaZrO}_3$ , barium aluminum spinel and Ag-coated substrates. Ag-coated substrates can include metals such as silver, ceramics, or composites. The method is equally applicable for substrates chemically inert or reactive with respect to the superconductor film.

When a substrate reacts with the resultant superconductor film, the atmosphere and heat treatment can be

selected to avoid the presence of a small amount of transient liquid phase thus avoiding reaction between the superconductor film and the substrate. Alternatively, when the substrate is not chemically reactive, the heat treatment and atmosphere can be selected to ensure that the actual amount of liquid phase is small, but of sufficient quantity to increase the grain growth rate to a rate adequate for creation of desired crystallographic texture. Multiple coatings can be made using fluorine containing precursor solutions and intermediate firings to produce mixed fluoride films sufficiently inert to withstand attack by an acid precursor solution.

The presence of a transient liquid phase during firing is encouraged by selection of processing atmosphere and temperature according to a phase diagram which includes the superconductor as well as all chemical constituents of the system. Temperature and oxygen partial pressure are chosen so that a liquid forms at points on the phase diagram corresponding to the compositions of local inhomogeneities in the coating, while, however, no liquid phase having a composition corresponding to the overall stoichiometry of the coating exists under these conditions, ensuring that the liquid phase is transient. Alternatively, atmosphere and temperature can be selected to avoid liquid containing phase fields between points in the phase diagram corresponding to compositions of the local inhomogeneities, thus ensuring that no liquid forms. The heat treatment consists of four steps. A first heating to a first temperature in a first controlled atmosphere decomposes the precursor coating while avoiding the volatilization of any precursor constituents. A second heating at a second temperature in a second controlled atmosphere creates compositional inhomogeneities in the coating. Processing at a third temperature in a third controlled atmosphere carefully selected to control the extent to which a small amount of transient liquid is present forms a compositionally homogeneous

film. The final heat treatment occurs at low temperature and high  $\text{PO}_2$  and ensures that the film is fully oxygenated. The first atmosphere can be moist oxygen, the second a moist reducing gas mixture, and the third dry oxygen depending upon the phase diagram of the system.

In one aspect of the invention, a  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  film is deposited on a (001) or (100) and preferably (100)  $\text{SrTiO}_3$  substrate from an organic solution containing metal trifluoroacetates prepared from powders of  $\text{BaCO}_3$ ,  $\text{YCO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{OH})_2\text{CO}_3$  combined and reacted in a 2:1:3 ratio with between 20-30% (5.5 - 6.0M) excess trifluoroacetic acid in methyl alcohol followed by refluxing for approximately four hours to produce a solution substantially 0.94 M based on copper content. This precursor solution is applied to a polished (001) or (100) and preferably (100)  $\text{SrTiO}_3$  substrate with a photoresist spinner operating at a speed in the range of approximately 3000-5000 rpm for a 0.25" x 0.25" substrate. Spin coating parameters can be adjusted to accommodate substrates of varying dimensions. The precursor coating is heated slowly at a rate approximately in the range of 0.5 to 1.0 °C/min in moist oxygen having a dew point approximately in the range of 20°C to 75°C to a temperature approximately in the range 300-500°C. After this heating step is complete, the coating is heated again for approximately one hour in a moist reducing nitrogen-oxygen gas mixture having a composition approximately in the range of 0.5 to 5.0% oxygen at a temperature less than 810°C. Following this heat treatment, the coating is cooled from the specified temperature range in dry oxygen for approximately 8 or more hours at a temperature in the range 400°C to 500°C.

In another aspect of the invention, a  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  superconductor film is fabricated on a  $\text{BaZrO}_3$  substrate. A metal trifluoroacetate precursor solution is mixed from powders of  $\text{BaCO}_3$ ,  $\text{YCO}_3 \cdot 3\text{H}_2\text{O}$  and

$\text{Cu}(\text{OH})_2\text{CO}_3$  combined in an approximately 2:1:3 ratio and reacted with 25-30% excess trifluoroacetic acid in methyl alcohol and refluxed for approximately ten hours to produce a viscous solution. A coating of the precursor is applied to a polished  $\text{BaZrO}_3$  substrate with a photoresist spinner at a speed approximately in the range of 3000-7500 rpm depending on substrate dimensions. The precursor coating is heated slowly, at a rate approximately in the range of 0.5 to 1.0°C/min in moist oxygen or nitrogen to a temperature in the range 300 to 500°C. Following this decomposition reaction, the coating is heated for one hour in moist oxygen or nitrogen or oxygen-nitrogen mixture at a temperature less than 860°C. In a final heat treating step, the coating is brought to a temperature higher than the second temperature approximately in the range of 860-950°C for a time approximately in the range of 5-25 minutes. The coating is cooled from this temperature range in flowing dry oxygen to a temperature approximately in the range of 400-500°C for eight or more hours. The film is cooled to room temperature in static dry oxygen.

A superconductor film prepared according to the method of the invention is characterized by a thickness in the range 0.1-2.0 microns, depending upon the concentration of the precursor and the spin coating parameters and is characterized by highly textured morphology and fully dense microstructure. Such a film is capable of sustaining critical current densities greater than  $10^4 \text{ A/cm}^2$  for films on non-lattice matched substrates or  $10^6 \text{ A/cm}^2$  for films on lattice matched substrates. In a preferred embodiment, the film has composition  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ .

The invention produces superior superconductor oxide thin films based on control of transient liquid phases during sintering. Superconducting oxide thin films having greatly enhanced texture with nearly equi-axed c-axis grains capable of supporting high current densities greater than  $10^4 \text{ A/cm}^2$  can be grown on non-lattice matched inert substrates.



Sintering atmosphere and temperatures as well as precursor solution composition are controlled such that production of a transient liquid phase during the sintering process is encouraged resulting in enhanced grain growth.

During growth of superconductor films on lattice matched substrates, not chemically inert with respect to the superconductor film, production of a transient liquid phase during sintering is undesirable since it speeds reaction between film and substrate. In this case, the film composition along with sintering atmosphere and temperatures are controlled to avoid formation of a transient liquid phase. If the substrate is also lattice matched to the superconductor oxide thin film, epitaxy contributes to production of a highly textured superconductor oxide film.

#### BRIEF DESCRIPTION OF THE DRAWING

In the drawing:

Fig. 1 is a temperature profile for initial calcination of a precursor coating;

Fig. 2 is a temperature profile for final calcination of the precursor coating to form the superconducting  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  film;

Fig. 3 are SEM photomicrographs of a film fired in 20°C dew point nitrogen at 850°C and then annealed in dry nitrogen at 920°C prior to cooling in oxygen;

Fig. 4 is an x-ray powder diffraction pattern of a film fired in 20°C dew point nitrogen heated to 850°C and then cooled in dry oxygen;

Fig. 5 is an x-ray powder diffraction pattern of a film heated to 850°C in moist nitrogen and then annealed in dry nitrogen at 920°C for fifteen minutes and cooled in oxygen;

Fig. 6 is an x-ray pole figure of a film fired in moist nitrogen for one hour at 850°C and then annealed in dry nitrogen for fifteen minutes at 920°C and cooled in dry oxygen;

Fig. 7 is a graph showing the voltage vs. temperature behavior of a film fired in moist nitrogen for one hour at 850°C and then annealed in dry nitrogen for fifteen minutes at 920°C and cooled in dry oxygen;

Fig. 8 is an illustration of the liquidus surface of the  $\text{YO}_{1.5}$ -BaO-CuO system showing the locus of compositions of films prepared according to the invention;

Fig. 9 is an SEM photomicrograph of a 0.4 micron-thick barium yttrium copper oxide film fired in moist oxygen at 850°C for one hour. Substrate was (100)  $\text{SrTiO}_3$ ;

Fig. 10 is an SEM photomicrograph of a 0.3 micron-thick barium yttrium copper oxide film fired in moist (75°C dew point)  $\text{N}_2/3.5\%\text{O}_2$  for one hour at 750°C on (100)  $\text{SrTiO}_3$ ;

Fig. 11 is an x-ray pole figure for the (103) barium yttrium copper oxide plane from a TFA-derived 0.3 micron-thick film fired in moist (75°C dewpoint)  $\text{N}_2/3.5\%\text{O}_2$  for one hour at 750°C (100)  $\text{SrTiO}_3$ .

Fig. 12 is an x-ray powder pattern for a 0.3 micron-thick barium yttrium copper oxide film fired in moist (75°C dew point)  $\text{N}_2/3.5\%\text{O}_2$  for one hour at 750°C (100)  $\text{SrTiO}_3$  substrate;

Fig. 13 is a graph showing the voltage vs. temperature behavior of a one micron thick film fired in moist  $\text{O}_2$  at 850°C for one hour on a (100)  $\text{SrTiO}_3$  substrate.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiments of the invention are described by way of the following examples which illustrate how according to the invention, superconductor thin films can be prepared on substrates having different characteristics selectively chosen to suit a particular application. According to the invention, superconductor thin films can be fabricated on lattice matched non-inert substrates such as  $\text{SrTiO}_3$  or can be fabricated on non-lattice matched inert substrates such as  $\text{BaZrO}_3$ .

EXAMPLE 1

Textured films of  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  can be grown on inert, non-lattice matched substrates such as  $\text{BaZrO}_3$  by processing precursor films at temperatures between 850°C and 920°C. C-axis texture is promoted by heat treatment and furnace atmosphere conditions which cause partial melting of Ba-Y-Cu-O compositions depleted in barium relative to  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ .

A metal trifluoroacetate (TFA) precursor solution was produced by mixing powders of  $\text{BaCO}_3$ ,  $\text{Y}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  in a 2:1:3 molar ratio and reacting them with 25% excess trifluoroacetic acid in the presence of methanol. The resulting solution was refluxed for approximately 10 h to react the starting materials completely and to concentrate the solution to a viscosity adequate for spin-coating. The solution was then centrifuged to extract any lint or other foreign particles present. Single coatings of precursor solution were spun onto  $\text{BaZrO}_3$  1-2 cm diameter substrates which had been prepared by slip-casting and firing to 1700°C for 6 h, resulting 95% approximate density as measured by water displacement. Fired substrates were ground flat and polished to a 0.25 micron diamond finish and subsequently etched for 15 min in 10% hydrofluoric acid (HF) prior to coating.

Green TFA films were calcined in two stages. A temperature profile for an initial calcination is shown in Fig. 1. In this calcination, the TFA precursor films were decomposed to mixed fluorides during slow heating (at a rate of 10°C/min) to 400°C in a moist oxygen atmosphere. The temperature profile for a typical final high temperature calcination is represented in Fig. 2. Flow of a moist nitrogen furnace atmosphere was initiated at 400°C. Films were heated in a moist atmosphere to 850°C at 10°C/min, and then held at 850°C for one hour. Following the one hour 850°C hold, the

furnace atmosphere was switched from moist to dry nitrogen, and the films were heated at 10°C/min to 920°C for a 15 min anneal. The films were slow cooled in dynamic dry oxygen to 400°C following the annealing step. At 400°C, the furnace was shut down and the films cooled to room temperature in a static oxygen atmosphere. All heat treatments were carried out in a CM 2200 quartz tube furnace. Moist furnace atmospheres were produced by bubbling the gas through an attached reservoir of deionized water prior to flowing through the furnace. The temperature of the reservoir was varied to control the partial pressure of water inside the furnace.

Phase development during calcination of the precursor was observed by TGA (Perkin Elmer TGA 7) and by x-ray diffraction with  $\text{Cu(K}_\alpha\text{)}$  radiation (Rigaku RU300 diffractometer). The microstructure of the fired BYC films was observed and characterized by scanning electron microscopy (SEM) (Hitachi S-530) and by x-ray pole figures (Rigaku RU200). Changes in film composition were characterized by Auger spectroscopy (Perkin Elmer 660 scanning Auger multiprobe), diffuse infrared Fourier transform spectroscopy (DRIFTS), and energy dispersive analysis by x-ray (EDAX). Electrical properties were determined directly by four-point DC current-voltage measurements. Wilver electrodes were deposited on the fired films by evaporation in a Denton DV-502A vacuum chamber. Following deposition of the electrodes, the films were annealed at 450°C for 2 h in oxygen to reoxygenate the material. Copper leads were joined to the electrodes with indium solder.

During the ramp from room temperature to 200°C, solvent was removed from the green precursor films. The films were heated very slowly from 200°C to 300°C to increase the duration of the TFA-fluoride decomposition which occurs over this temperature range. Faster heating rates (greater than 1°C/min) lead to the development of large cracks in the

calcined films. A moist oxygen atmosphere was used in the low temperature calcination to prevent the loss of copper during heating of mixed TFA films in dry furnace atmospheres. Films prepared from TFA solutions and calcined to 400°C in dry oxygen were transparent and, after subsequent high temperature treatments, showed no sign of BYC by x-ray diffraction. Examination of the composition of these films using EDAX indicated a complete absence of copper. Copper depletion was not observed when the low temperature calcination was performed under a moist oxygen atmosphere.

The furnace atmosphere was found to have a significant effect on the final film morphology and properties. When a moist oxygen atmosphere was used during the high temperature calcination, a microstructure consisting of randomly-oriented BYC platelets resulted and did not appear to change significantly during the hold at 850°C or during the subsequent anneal at 920°C. The platelet morphology had substantial open porosity, and the electrical transport properties of these films were poor with no superconducting transition observed. x-ray powder diffraction indicated no preferred orientation of the BYC crystallites in these films. Films calcined above 800°C in moist nitrogen, however, were dense, c-axis textured, and had improved electrical transport properties. The photomicrograph in Fig. 3 shows the rather featureless appearance of these films; there is an absence of porosity other than flaws associated with surface pores in the  $\text{BaZrO}_3$  substrates. The x-ray powder diffraction pattern and x-ray pole figure for the pictured film (Figs. 4, 5 and 6) indicate a high degree of c-axis preferred orientation. The voltage-temperature behavior of this film is shown in Fig. 7. In contrast to the films fired in moist oxygen, metallic behavior was observed before the transition, which was fairly sharp ( $T_c(\text{onset})=90\text{K}$   $T_c(0)=80\text{K}$ ). The observed  $J_c(4.2\text{K})$  values for films given this heat treatment (850°C: 1 h,

$\text{N}_2/\text{H}_2\text{O}$  920°C: 15 min,  $\text{N}_2$ ) were approximately 2000  $\text{A}/\text{cm}^2$ . Measured room temperature resistivities for these films were less than  $10^{-3}$  ohm-cm.

The effect of the heat treatment on texture development is shown in Fig. 4 and 5. The degree of c-axis texture can be assessed qualitatively by comparing the intensity of the (00 $l$ ) reflections to that of the (110) peak, which is the strongest reflection for a randomly-oriented sample of  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ . The x-ray powder diffraction pattern in Fig. 3 represents the case of a TFA-derived film that was heated to 850°C in moist (20°C dew point) nitrogen and then immediately cooled in dry oxygen. The presence of reflections associated with  $\text{BaF}_2$ ,  $\text{Y}_2\text{O}_3$ , and  $\text{CuO}$  indicate that fluoride decomposition was not yet complete, and BYC phase formation was just beginning when 850°C was reached. Fig. 5 shows the effect of adding a 15 minute anneal at 920°C in nitrogen to the heat treatment described above. In this case, significant BYC formation took place and much of the phase appeared to have a preferred c-axis orientation. Comparison of BYC peak intensities indicated that texture development occurred during the nitrogen anneal at 920°C, but it was limited due to the fact that a large fraction of the barium remained as  $\text{BaF}_2$  and was not available to form  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ . In films that were held at 850°C in 20°C dew point nitrogen for 1 hour and then cooled in oxygen, no  $\text{BaF}_2$  can be detected and fairly broad peaks corresponding to the (003), (005), and (006) BYC reflections are visible in the diffraction pattern indicating some c-axis texture. In addition, the  $\text{Y}_2\text{O}_3$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ , and  $\text{CuO}$  reflections demonstrate that regions of the films were barium-depleted after firing at 850°C for 1 hour. The addition of a 15 minute 920°C anneal in nitrogen to the 1 hour hold in moist nitrogen at 850°C produced a dramatic increase in the degree of texture present in the films (Fig. 4). The "shoulder" on the low-angle side of the main  $\text{BaZrO}_3$  reflection in the pattern suggests that  $\text{Y}_2\text{O}_3$  was present, and this conclusion is supported by the existence of a low intensity  $\text{CuO}$  peak.

In addition to the heat treatments in 20°C dew point nitrogen furnace gas, a number of films were fired in higher  $P_{H_2O}$  atmospheres by heating the water reservoir through which the gas bubbled. As in the lower moisture case, enhanced c-axis texture was observed in these heated-reservoir films following a 920°C anneal in dry nitrogen (see Figs. 10a and 10b). However, growth of c-axis textured BYC also took place when the furnace gas was switched to dry oxygen for the anneal, after the preceding 850°C hold was performed in 75°C dew point nitrogen. Fig. 6 represents an x-ray pole figure of a highly textured film produced using an oxygen anneal. In the low  $P_{H_2O}$  case, annealing in oxygen produced films with little or no texture and with platelet microstructure..

A summary of heat treatments and their effect on the degree of c-axis orientation in the films is presented in Table I below.

Table I. Summary of Heat Treatments and C-axis Texture in TFA-derived Films.

Hold gas (wet)	Hold time (h)	Dew Point (°C)	Anneal gas	Texture	BaF <sub>2</sub>
O <sub>2</sub>	3	75	O <sub>2</sub>	None	no
O <sub>2</sub>	1	75	n.a.	None	no
O <sub>2</sub>	*	75	n.a.	None	no
N <sub>2</sub>	3	75	O <sub>2</sub>	Strong	no
N <sub>2</sub>	1	75	N <sub>2</sub>	Strong	no
N <sub>2</sub>	1	75	n.a.	Weak	no
N <sub>2</sub>	*	75	n.a.	Weak	no
N <sub>2</sub>	1	20	O <sub>2</sub>	None	no
N <sub>2</sub>	3	20	N <sub>2</sub>	Strong	no
N <sub>2</sub>	1	20	N <sub>2</sub>	Strong	no
N <sub>2</sub>	1	20	n.a.	Weak	no
N <sub>2</sub>	*	20	n.a.	None	yes
N <sub>2</sub>	*	20	N <sub>2</sub>	Moderate	yes

\*these films were heated to 850°C in moist furnace atmospheres and then immediately cooled in dry O<sub>2</sub>.

A schematic representation of the ternary system BaO-YO<sub>1.5</sub>-CuO near CuO is shown in Fig. 8 (J.E. Ullman, R.W. McCallum et al., J. Mater. Res. 4, 752-754 (1989)). The locus of compositions investigated for partial melting is shown as the dashed line running from Ba<sub>2</sub>YCu<sub>3</sub>O<sub>7-x</sub> to the YO<sub>1.5</sub>-CuO binary. A summary of the partial melting temperatures observed as a function of barium depletion and atmosphere is provided in Table II.

Table II. Observed DTA Melting Endotherm Onset Temperatures as a Function of Barium Content and Atmosphere.

Mol% Ba Deficiency	DTA Melting Onset Temperatures (°C)	
	O <sub>2</sub> Atmosphere	N <sub>2</sub> /H <sub>2</sub> O Atmosphere
0	1010	955
5	957	859
10	964	861
20	960	855
40	960	860
60	963	864
80	988	863
100	1085	910-950

A moist nitrogen atmosphere was chosen to simulate the furnace atmosphere used during the high temperature calcination of the films produced in this study.

The introduction of moisture during both stages of calcination of the TFA-derived films had important consequences for film composition and microstructure development.



The removal of copper from the green films during low temperature calcination in a dry furnace atmosphere is attributed to the volatilization of  $\text{Cu}(\text{TFA})_2$ . It is believed that hydrolysis of  $\text{Cu}(\text{TFA})_2$  to non-volatile  $\text{Cu}(\text{TFA})(\text{OH})$  took place when the initial calcination was performed in a moist furnace atmosphere.

In high temperature calcinations, water vapor in the furnace gas reacted with  $\text{BaF}_2$ ,  $\text{YF}_3$ , and  $\text{CuF}_2$  to form the mixed metal oxides and HF gas. The x-ray diffraction pattern in Fig. 4 indicates that yttrium and copper fluoride were completely converted to their respective oxides below  $850^\circ\text{C}$  by reaction with water vapor. However,  $\text{BaF}_2$  was present in the films up to  $850^\circ\text{C}$  and beyond, depending upon the duration of the heat treatment in  $20^\circ\text{C}$  dew point furnace gas. Changing the moist furnace gas from nitrogen to oxygen did not appear to affect the degree of  $\text{BaF}_2$  removal. Heating the water reservoir to  $75^\circ\text{C}$  caused the elimination of  $\text{BaF}_2$  at furnace temperatures below  $850^\circ\text{C}$  as observed by x-ray diffraction and Auger spectroscopy.

A DTA study indicates that partial melting of barium-deficient  $\text{Ba-Y-Cu-O}$  compositions may occur at temperatures as low as  $860^\circ\text{C}$ , which is within the temperature range used in firing the TFA-derived films. The stability of  $\text{BaF}_2$  above  $800^\circ\text{C}$  causes inhomogeneities in composition during high temperature calcination of the films. Before reaction of the fluorides with water vapor is complete, the films may consist of grains of  $\text{BaF}_2$  in a barium-depleted matrix. The x-ray diffraction results in Fig. 5 indicate that localized barium depletion persisted after the  $\text{BaF}_2$  had been completely decomposed. Presumably, elimination of local compositional variations is limited by the rates of interdiffusion of  $\text{BaO}$  and the barium-deficient material, and the rate of reaction of the oxides to form  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$ . Evidently, the heat treatments used in this work did not fully eliminate local

compositional variations, and regions of the films remained barium-deficient throughout the high temperature calcination. Therefore, the DTA results suggest that a liquid phase may form transiently in the TFA-derived BYC films during the annealing step at 920°C in a reducing atmosphere.

The increase in c-axis preferred orientation observed when the films were annealed in nitrogen at 920°C occurred under conditions in which DTA experiments suggest melting of the barium-depleted material should take place. This implies that texture development in this system may be linked to the presence of a liquid phase at high temperatures. The presence of a small amount of liquid phase during the firing of ceramic materials can assist in the formation of large grains through secondary recrystallization (W.D. Kingery et al., Introduction to Ceramics; (John Wiley & Sons, New York, NY, 1976), pp.461-465). A correlation between partial melting and texture development is consistent with the observation that a random microstructure formed when the TFA-derived films were fired in moist oxygen. The DTA experiments indicate that firing under oxidizing conditions will not promote melting of barium-depleted film material at the calcination temperatures used in this study.

Results obtained in DTA experiments do not seem to support the formation of a liquid phase when the 920°C anneal is performed in oxygen. The random orientation of BYC platelets observed is consistent with DTA results. In that case, the film was held at 850°C in 20°C dew point nitrogen before being annealed in dry oxygen at 920°C. However, when films were exposed to 75°C dew point nitrogen prior to the oxygen anneal, strong c-axis texture resulted. Clearly, the amount of water vapor present in the furnace has a significant effect on the degree of texture that is developed during the annealing step in these particular heat treatments. When oxygen flow began at the end of the 850°C hold, there was an

exchange time before the moist reducing atmosphere was fully replaced by dry oxygen. We believe that nitrogen and water vapor persisted in the furnace atmosphere to temperatures greater than 900°C prior to the start of the anneal. The effect of a complex  $N_2/H_2O/O_2$  atmosphere on the peritectic melting temperatures in the  $BaO-YO_{1.5}-CuO$  ternary system can lead to formation of a small amount of liquid phase when the films are heated to 920°C, before oxygen becomes the dominant component in the furnace gas.

#### EXAMPLE II

A  $Ba_2Cu_3O_{7-x}$  film was prepared on a (100)  $SrTiO_3$  substrate by MOD of metal trifluoroacetate precursors.  $SrTiO_3$  is lattice matched to  $Ba_2YCu_3O_{7-x}$ , but is not chemically inert with respect to this compound. A low temperature processing technique for growth of  $Ba_2YCu_3O_{7-x}$  avoids the formation of a transient liquid phase which might react with the  $SrTiO_3$  substrate, resulting in formation of undesirable reaction products. The reaction proceeds by the formation of the more stable barium titanium oxide and subsequent depletion of the film of barium and contamination of the film with strontium. Film texture development is encouraged through epitaxy.

A film was prepared by spin coating a (100)  $SrTiO_3$  substrate with a precursor solution of the mixed Ba, Y, and Cu TFA salts in methanol. The TFA precursor solution was produced by mixing powders of  $BaCO_3$ ,  $Y_2CO_3 \cdot 3H_2O$ , and  $Cu_2(OH)_2CO_3$  in a 2:1:3 ratio and reacting them with 25% excess trifluoroacetic acid in methyl alcohol. The mixed solution was refluxed for 4 h to completely react the starting materials. Single coatings of this approximately 0.94M based on Cu concentration solution were applied to polished (100)  $SrTiO_3$  single crystal substrates (.25 in x .25 in x .02 in) with a photoresist spinner operating at 4000 rpm.

The film was fired in two stages. The first stage was a slow calcination ( $0.5^{\circ}\text{C}/\text{min}$ ) in moist ( $20^{\circ}\text{C}$  dew point) oxygen to  $400^{\circ}\text{C}$ . The resulting oxyfluoride film was transparent and appeared to be uniform in thickness. The second stage of the heat treatment was a 1 hour hold in moist ( $75^{\circ}\text{C}$  dew point) nitrogen/3.5% oxygen at  $750^{\circ}\text{C}$ . Oxygen was added to the reducing gas mixture to insure stability of the tetragonal BYC phase at high temperature. High  $P_{\text{H}_2\text{O}}$  was required to convert  $\text{BaF}_2$  to the oxide at  $750^{\circ}\text{C}$  (rather than at  $850^{\circ}\text{C}$  as in previous runs). Lowering the hold temperature from  $850^{\circ}\text{C}$  to  $750^{\circ}\text{C}$  prevented film/substrate reactions that had been observed in earlier films fired on  $\text{SrTiO}_3$  in reducing conditions. The film was cooled from  $750^{\circ}\text{C}$  in dry oxygen with an eight hour hold at  $450^{\circ}\text{C}$ . All heat treatments were carried out in a CM 2200 quartz tube furnace. Moist furnace atmospheres were produced by bubbling the gas through an attached heated reservoir of deionized water prior to flowing through the furnace.

Fig. 9 shows a microstructure of aligned grains indicating registration of the barium yttrium copper oxide lattice with the substrate for a film fired in moist oxygen at  $850^{\circ}\text{C}$  for 1 hour. Processing a superconductor film at a temperature lower than  $850^{\circ}\text{C}$  in a reducing atmosphere can remove this "patchwork" texture by suppressing the formation of a-axis perpendicular to the substrate. The x-ray pole figure shown in Fig. 11 indicates an epitaxial relationship exists between the superconductor film and the substrate. The x-ray powder pattern shown in Fig. 12 shows only film and substrate reflections for 00n planes, indicating that the formation of a-axis perpendicular to the substrate has been suppressed and corroborating the microstructural evidence of Fig 10.

This processing resulted in a film with very good electrical transport properties. The measured critical current density was in excess of  $10^6 \text{ A}/\text{cm}^2$  at 77 K in zero applied field. The  $T_c$  (zero resistance) equals 92K with a transition width of 2-3 K, as shown in Fig. 12.

What is claimed is:

1. A method for fabricating a superconducting oxide film comprising:

preparing a precursor solution containing cation constituents of the film in a stoichiometry nearly equal to the stoichiometry of the oxide film;

applying a coating of the precursor solution to a substrate;

exposing the coating to heat treatment in a selected atmosphere to control the presence of a transient liquid phase during firing to produce the superconducting oxide film.

2. The method of claim 1 wherein the presence of the transient liquid phase is desirable and the superconductor oxide is included in a phase diagram containing points where selected heat treatment and atmosphere correspond to a liquid phase between compositions characteristic of coating local inhomogeneities and where a phase having the same overall stoichiometry of the coating is not liquid under these conditions.

3. The method of claim 1 wherein the precursor solution contains an organic compound.

4. The method of claim 3 wherein the precursor solution contains an organic metal salt and is capable of forming a film having the overall stoichiometry of the superconductor, but having small regions inhomogeneous in composition such as a metal trifluoroacetate and chloroform, methyl alcohol or other alcohol solution.

5. The method of claim 1 wherein the precursor solution is applied to a spinning substrate.

6. The method of claim 1 wherein the precursor solution is applied to the substrate by dipping the substrate into the solution, or spraying or printing the solution onto the substrate surface.

7. The method of claim 1 wherein the substrate is flat.
8. The method of claim 1 wherein the substrate is three-dimensional.
9. The method of claim 8 wherein the three dimensional substrate is a ribbon, wire or coil.
10. The method of claim 1 wherein the substrate is a single crystal lattice-matched to the superconductor film.
11. The method of claim 1 wherein the substrate is not lattice-matched to the superconductor film.
12. The method of claim 1 wherein the substrate is chemically inert with respect to the superconductor film.
13. The method of claim 1 wherein the substrate is not chemically inert with respect to the superconductor film.
14. The method of claim 10 wherein the lattice-matched substrate is a lattice-matched substrate selected from the group consisting of (001)  $\text{SrTiO}_3$ , (001)  $\text{LaAlO}_3$ , (001)  $\text{LaGaO}_3$ , and (001)  $\text{NdGaO}_3$ .
15. The method of claim 11 wherein the non-lattice matched substrate is a non-lattice matched substrate selected from the group consisting of  $\text{BaZrO}_3$ , Ag-coated metal, ceramic or composite substrates, and barium aluminum spinel.
16. The method of claim 12 wherein the chemically inert substrate is  $\text{BaZrO}_3$ .

17. The method of claim 13 wherein the non-chemically inert substrate is selected from the group consisting of  $\text{SrTiO}_3$ ,  $\text{LaAlO}_3$ ,  $\text{LaGaO}_3$ , and  $\text{NdGaO}_3$ .

18. The method of claim 1 wherein the heat treatment and atmosphere are selected to minimize the presence of the transient liquid phase.

19. The method of claim 1 wherein the heat treatment and atmosphere are selected to ensure that the actual amount of transient liquid phase is small, but large enough to increase the rate of grain growth to create crystallographic texture.

20. The method of claim 1 wherein multiple applications of precursor solution are made followed by intermediate firings to produce a multilayer coating.

21. The method of claim 1 wherein the precursor solution wets the substrate well enough to coat the substrate.

22. The method of claim 1 wherein the cations are chosen from the group consisting of La, Ba, Cu, Y, Sr, Ca and rare-earth ions such as Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Pr, Ce, and Lu.

23. The method of claim 1 wherein the cation constituents are introduced as compounds chosen from the group consisting of soluble carbonate, hydroxide, acetate salts of La, Ba, Cu, Y, Sr, Ca, Eu, Gd, Th, Dy, Ho, Er, Tm, Yb, Pr, Ce, and Lu.

24. The method of claim 23 wherein the barium, yttrium, and copper containing salts are in a 2:1:3 ratio.

25. The method of claim 1 wherein the coating has the overall stoichiometry of the superconductor, but has small regions inhomogeneous in composition.

26. The method of claim 1 wherein atmosphere and temperature are selected so that a liquid containing phase field appears in a phase diagram which includes the superconductor oxide between points in the phase diagram which correspond to compositions of local inhomogeneities in the coating, while a point in the phase diagram corresponding to overall coating stoichiometry does not contain a liquid at said atmosphere and temperature.

27. The method of claim 1 wherein atmosphere and temperature are chosen so that no liquid containing phase field exists in a superconductor phase diagram between points corresponding to compositions of local coating inhomogeneities.

28. The method of claim 1 wherein the heat treatment consists of four steps, a first heating at a first temperature in a first controlled atmosphere to decompose the precursor coating while avoiding the volatilization of a metal containing precursor constituent; a second heating at a second temperature in a second controlled atmosphere to create local compositional inhomogeneities in the coating; processing at a third temperature in a third controlled atmosphere carefully selected to control the extent to which a small amount of transient liquid is present and to form a compositionally homogeneous film; and final heat treatment at low temperature and high  $PO_2$  to insure that the film is fully oxygenated.

29. The method of claim 28 wherein the first controlled atmosphere is a moist gas, the second a moist reducing gas mixture and the third dry oxygen.



30. A method for fabricating a  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  superconductor film on a (100)  $\text{SrTiO}_3$  substrate comprising:

mixing a metal trifluoroacetate precursor solution from powders of  $\text{BaCO}_3$ ,  $\text{YCO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{OH})_2\text{CO}_3$  in an approximately 2:1:3 ratio and reacting them with between 20% and 30%, 5.5-6.0 M excess trifluoroacetic acid in methyl alcohol, followed by refluxing for approximately four hours to produce a solution substantially 0.94 M based on copper content;

applying a coating of the precursor solution to a polished (100)  $\text{SrTiO}_3$  substrate with a photoresist spinner at a speed in the range of approximately 3000-5000 rpm depending on substrate dimensions;

heating the coating slowly, at a rate approximately in the range of  $0.5-1.0^\circ\text{C}/\text{min}$ , in moist oxygen having a dew point approximately in the range of  $20-75^\circ\text{C}$  to a temperature approximately in the range  $300-500^\circ\text{C}$

heating the coating for approximately one hour in moist reducing nitrogen/oxygen gas mixture, having a composition approximately in the range of 0.1-5%  $\text{O}_2$  at a temperature below  $810^\circ\text{C}$ ;

cooling the coating from said temperature range in dry oxygen with a hold for a time in excess of 2 hours at temperatures approximately in the range  $400-500^\circ\text{C}$ .

31. A method for fabricating a  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  superconductor film on a  $\text{BaZrO}_3$  substrate comprising:

mixing a metal trifluoroacetate precursor solution from powders of  $\text{BaCO}_3$ ,  $\text{YCO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Cu}(\text{OH})_2\text{CO}_3$  in an

approximately 2:1:3 ratio and reacting them with 5.5-6.0 M excess trifluoroacetic acid in methyl alcohol, followed by refluxing for approximately ten hours to produce a viscous solution;

applying a coating of the precursor to a polished  $\text{BaZrO}_3$  substrate with a photoresist spinner at a speed approximately in the range of 3000-7500 rpm depending on substrate dimensions;

heating the coating slowly, at a rate approximately in the range of  $0.5-1.0^\circ\text{C}/\text{min}$ , in moist oxygen or nitrogen to a temperature in the range of  $300-500^\circ\text{C}$ ;

heating the coating for a time approximately in the range of 0.25-4.00 hour in moist oxygen or nitrogen at a temperature approximately in the range of  $650-850^\circ\text{C}$ ;

heating the coating at a rate approximately in the range of  $5-20^\circ\text{C}/\text{min}$  to a temperature approximately in the range of  $860-950^\circ\text{C}$  for a time approximately in the range of 5-30 minutes;

cooling the coating from said temperature range in flowing dry oxygen to a temperature approximately in the range of  $400-500^\circ\text{C}$ ;

further cooling the coating to room temperature in static dry oxygen.

32. A superconducting oxide film fabricated by the method of any of claims 1-32.

33. A superconductor oxide film on a non-lattice matched substrate having a thickness in the range 0.1-2.0 microns, characterized by a highly textured morphology and fully dense microstructure capable of sustaining critical current densities greater than  $10^4 \text{ A}/\text{cm}^2$ .

34. A superconductor oxide film on a lattice matched substrate having a thickness in the range 0.1-2.0 microns characterized by a highly textured morphology and fully dense microstructure and capable of sustaining critical current densities greater than  $10^6$  A/cm<sup>2</sup>.

35. A  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  superconductor oxide film on a non-lattice matched substrate having a thickness in the range 0.1-2.0 microns, characterized by a highly textured morphology and fully dense microstructure capable of sustaining critical current densities greater than  $10^4$  A/cm<sup>2</sup>.

36. A  $\text{Ba}_2\text{YCu}_3\text{O}_{7-x}$  superconductor oxide film on a lattice matched substrate having a thickness in the range 0.1-2.0 microns characterized by highly textured morphology and fully dense microstructure capable of sustaining critical current densities greater than  $10^6$  A/cm<sup>2</sup>.

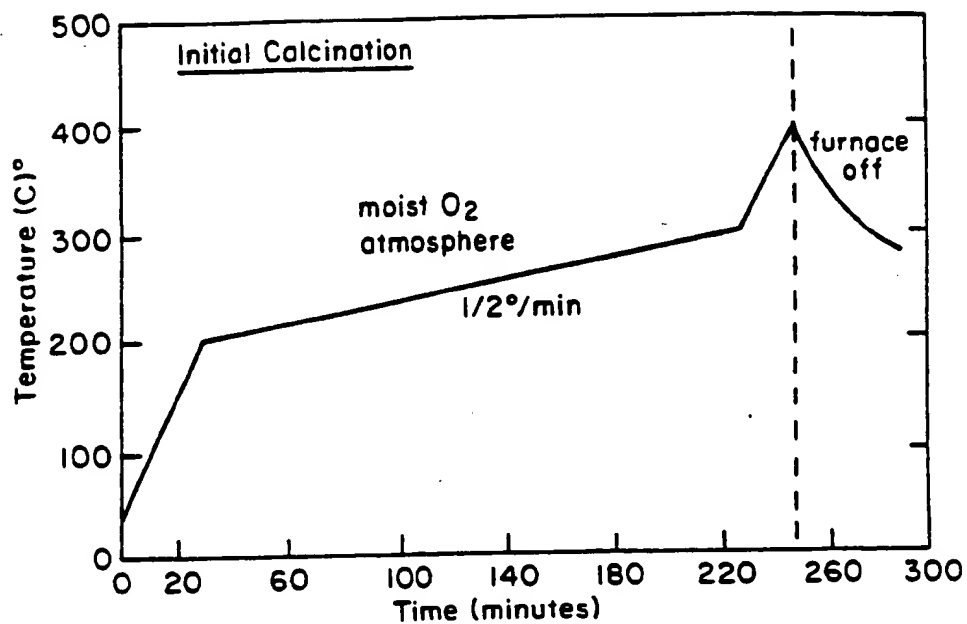


FIG. 1

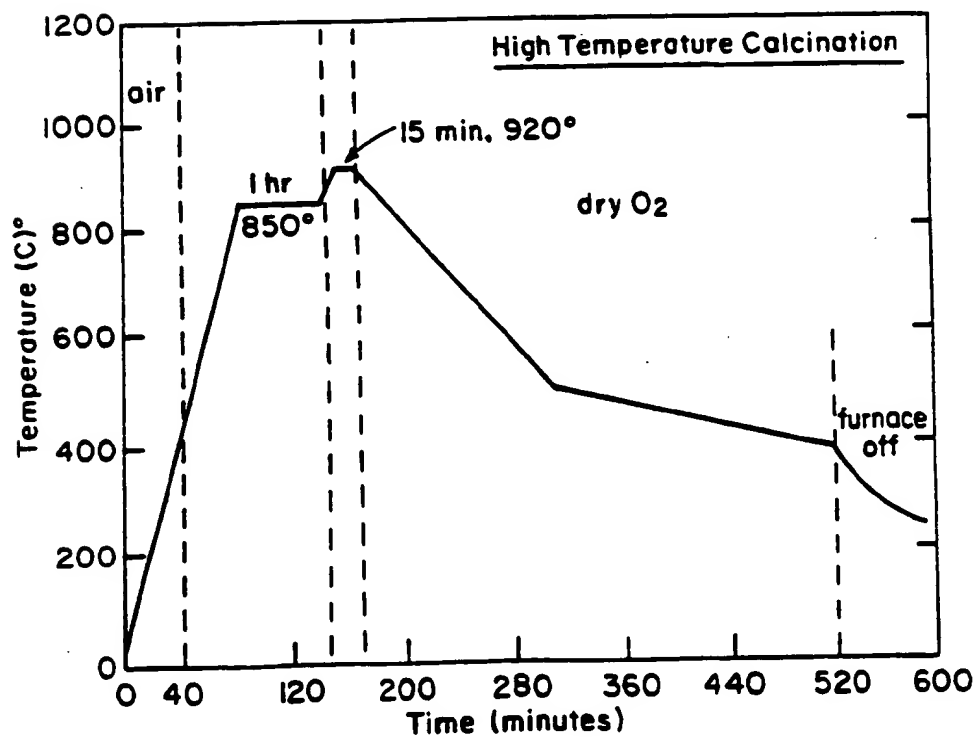
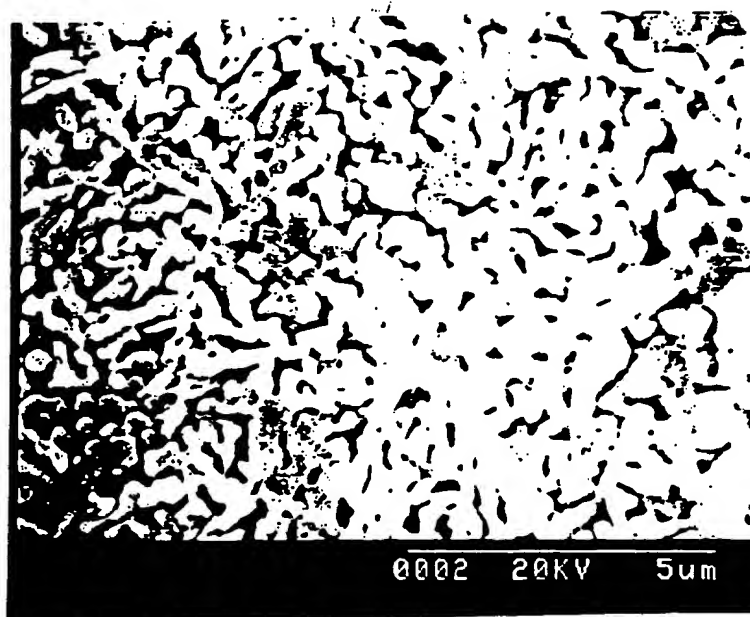
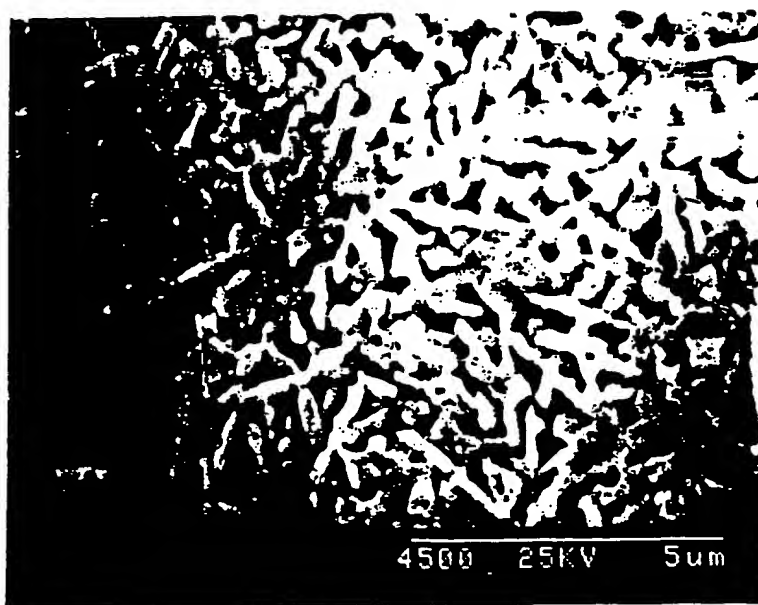


FIG. 2

2 / 8



**FIG. 3A**



**FIG. 3B**

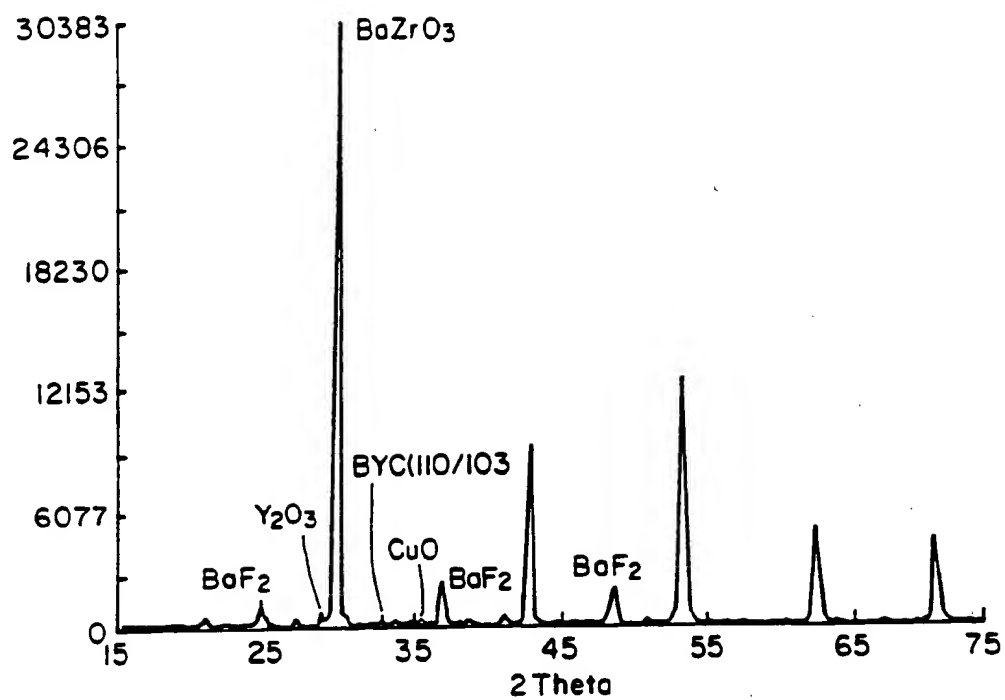


FIG. 4

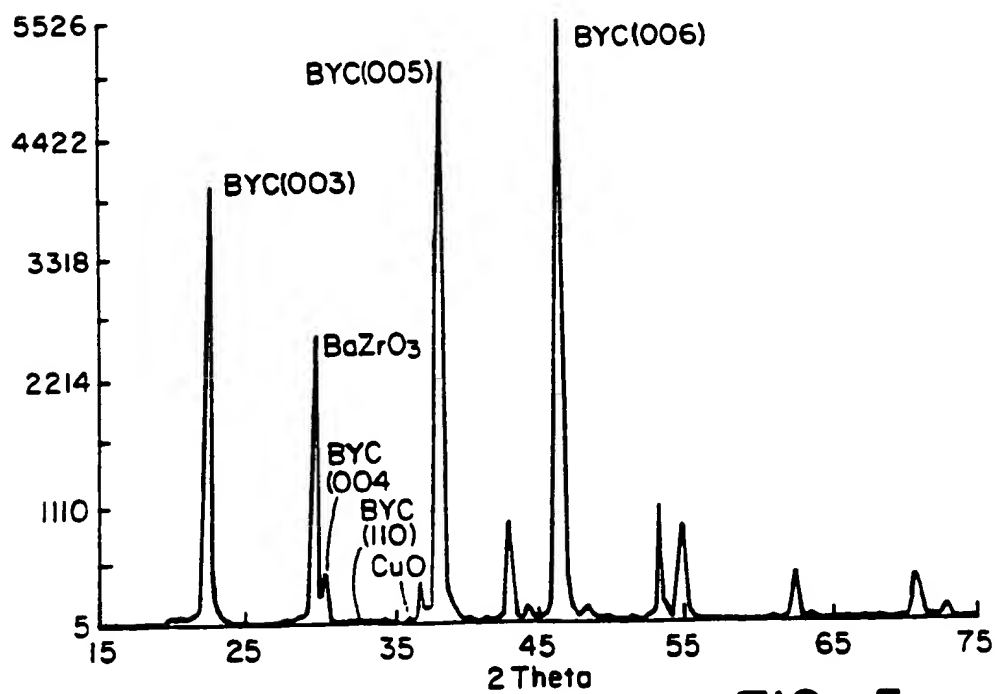


FIG. 5

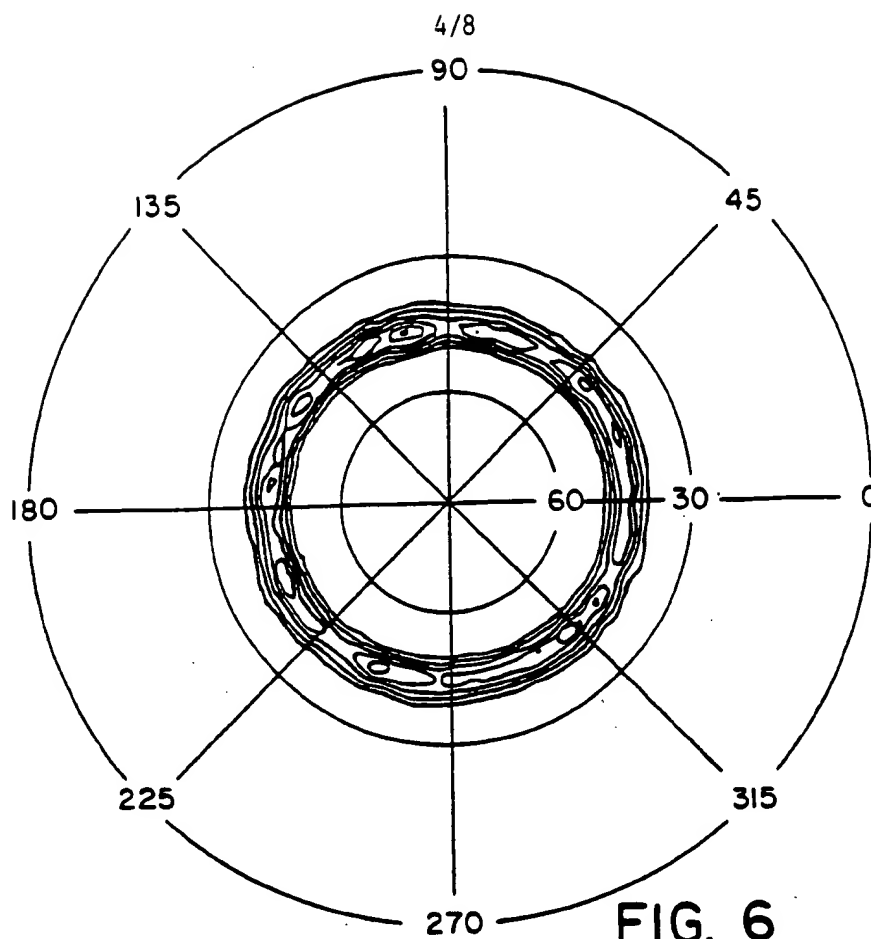


FIG. 6

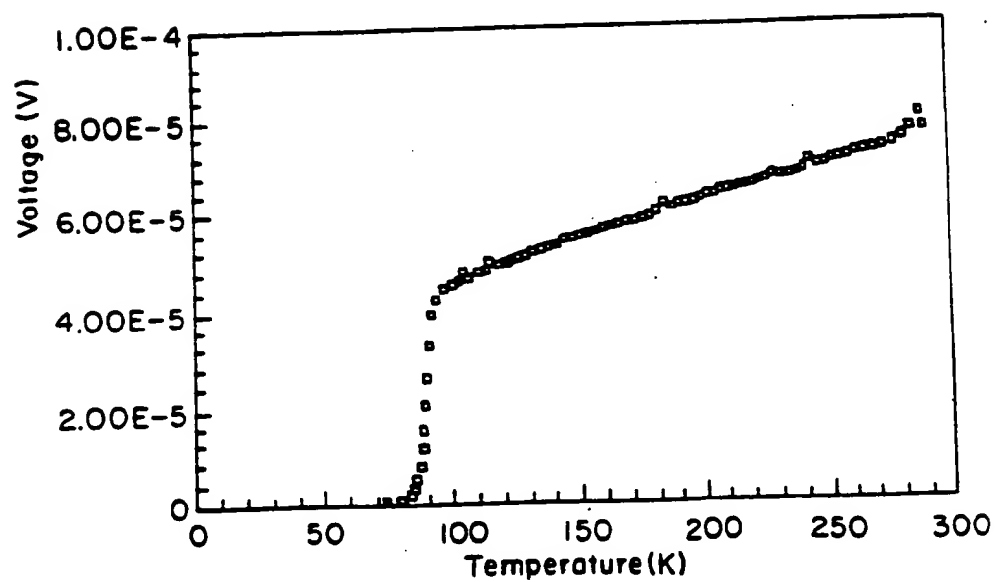


FIG. 7

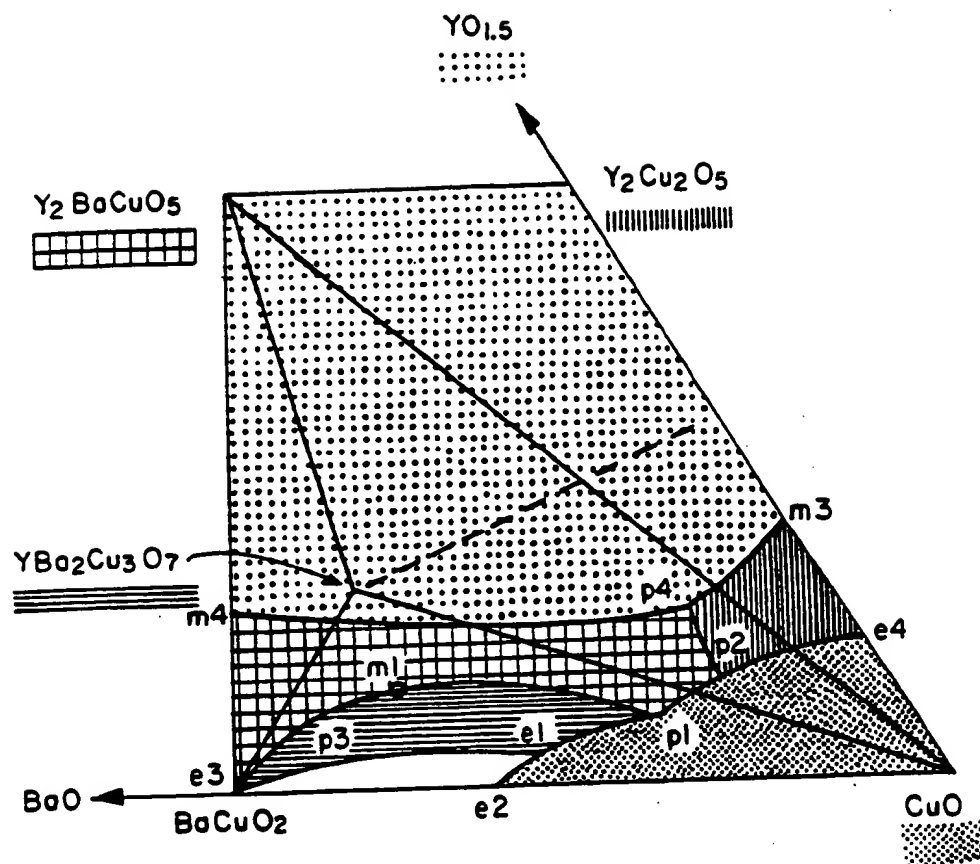


FIG. 8



6 / 8

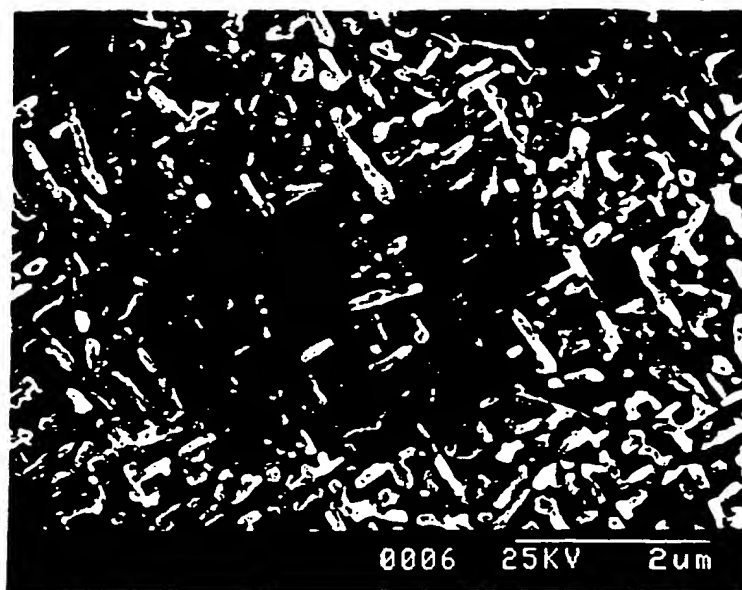


FIG. 9

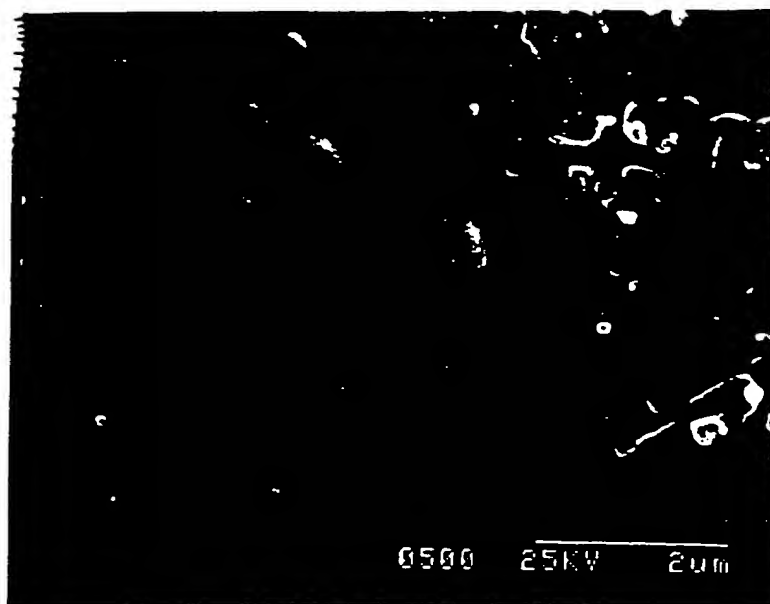


FIG. 10

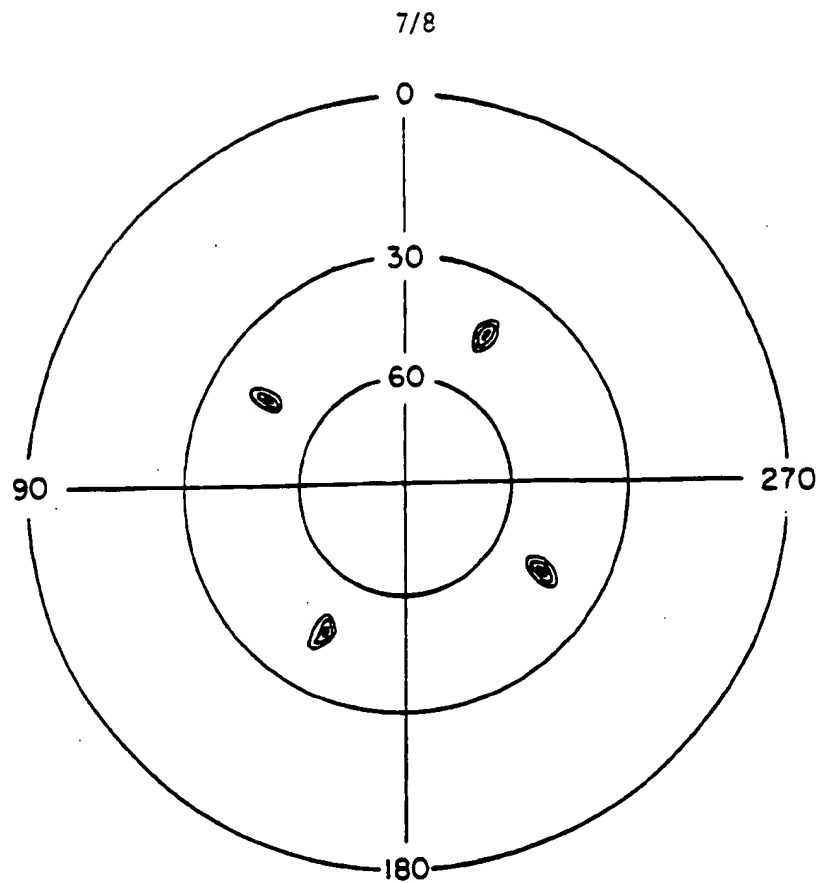


FIG. 11

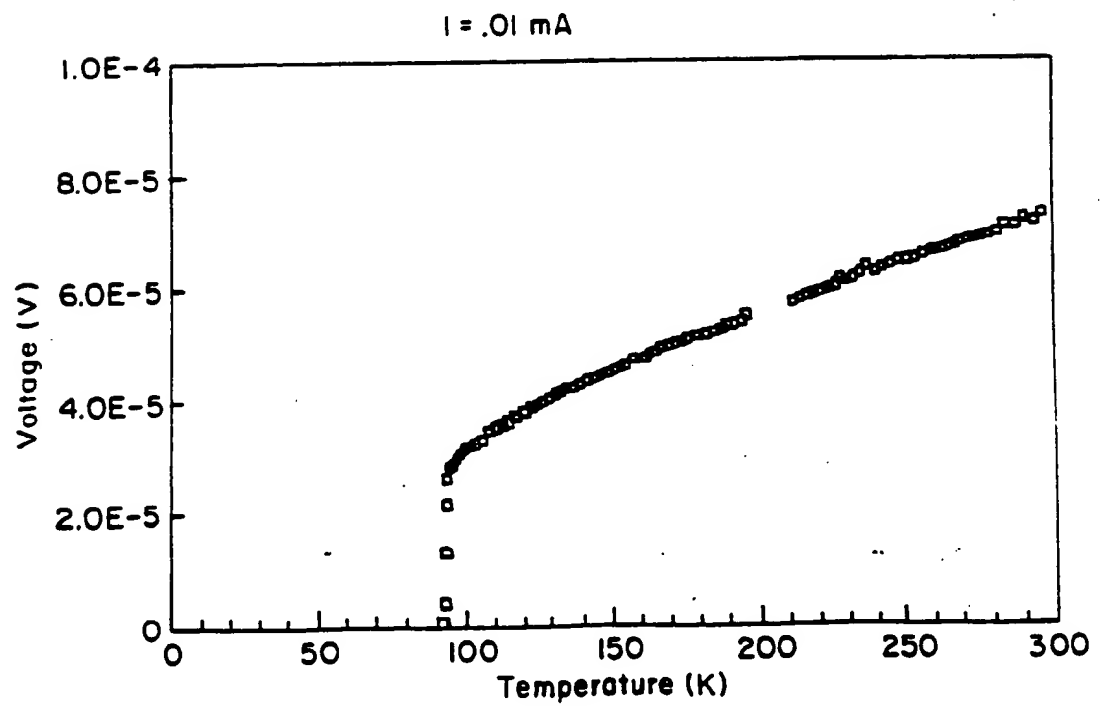


FIG. 13

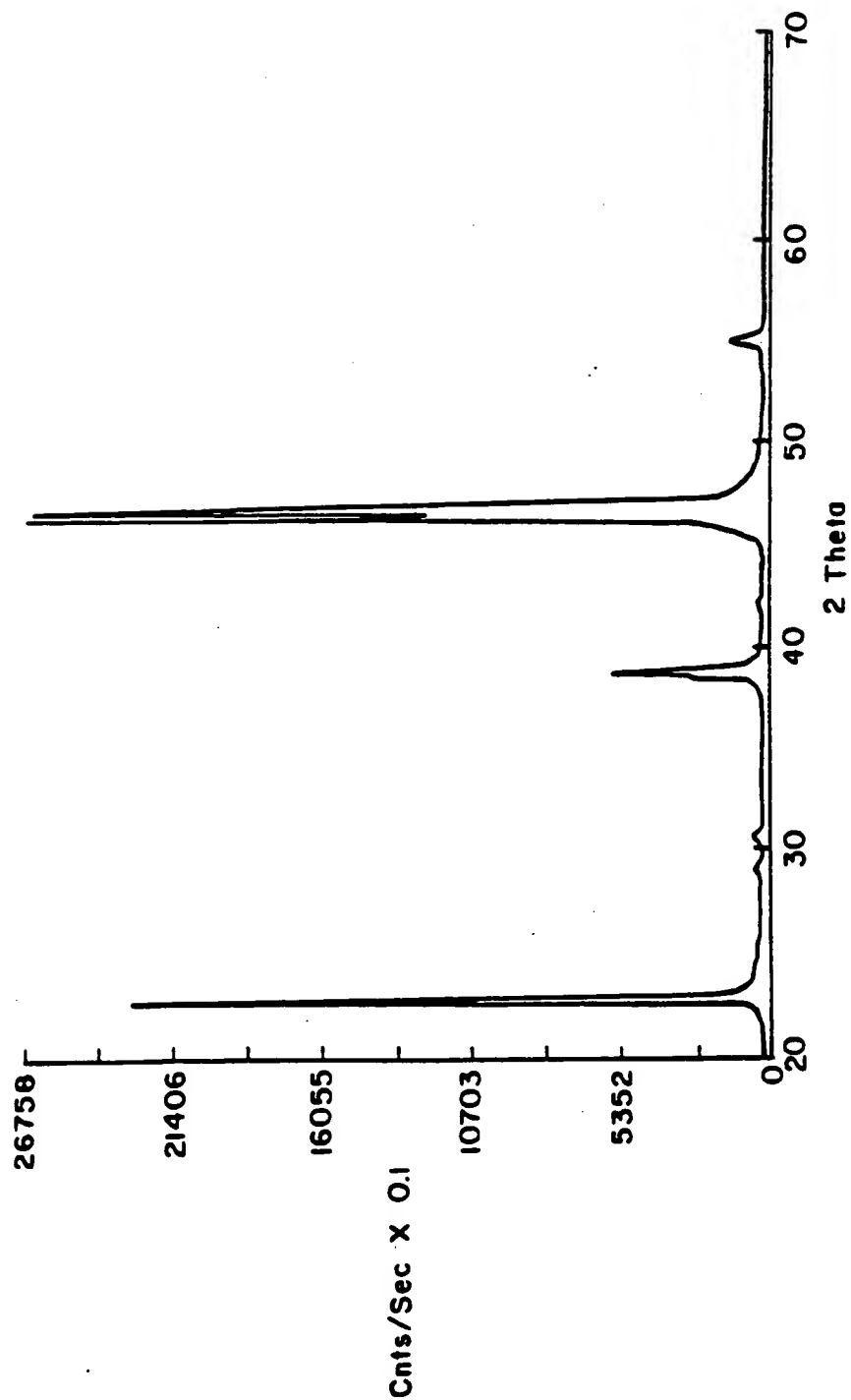
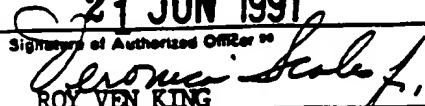


FIG. 12

SUBSTITUTE SHEET

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/01791

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all)		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): B05D 5/12, 3/02 U.S. CL.: 505/734, 427/62, 226		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched *		
Classification System:	Classification Symbols:	
U.S.	505/1, 505/734 427/62, 63, 226, 126.3	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of Document, 16 with indication, where appropriate, of the relevant passages 17	Relevant to Claim No. 18
Y	MRS Bulletin, Issued October 1989, Martese et al "metalorganic Deposition (MOD): A non-vacuum spin-on, liquid-based, thin film method" (See pages 48-53).	1-32, 34, 36
Y	Appl. Phys. Lett, Volume 51. No. 25, Issued December 1987, Hamdi et al, Formation of thin- film high Tc superconductors by metalorganic deposition" (See pages 2152-2154).	1-32, 34, 36
Y	Jpn. J. Appl. Phys. Volume 27, No 9, Issued September 1988, Komatsu et al "On the new substrate materials for High-Tc superconducting barium Yttrium Copper oxide thin-films" (See L1686-1689).	11-12, 15-16 31-32, 33, 35
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: 16</p> <p>"A" document disclosing the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"A" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search *	Date of Mailing of this International Search Report *	
16 MAY 1991	21 JUN 1991	
International Searching Authority:	Signature of Authorized Officer **	
ISA/US	 ROY VEN KING	

Form PCT/ISA/210 (second sheet) (May 1988)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages **	Relevant to Claim No. 1 *
Y	Appli. Phys. Lett. Volume 51. No. 22, Issued November 1987, Rice et al, "Preparation of Supersconducting thin films of $\text{Ba}_2\text{YCu}_3\text{O}_7$ by a novel spin-on pyrolysis technique" (See pages 1842-1844).	30-32
Y	Appl. Phys. Lett. Volume 52. No. 24, Issued June 1988, Gupta et al, "Superconducting Oxide films with high transition temperature prepared from trifluoroacetate precursors" (See pages 2077-2079).	30-32
Y	Appl. Phys. Lett. Volume 51. No 23, Issued November 1987, Mankiewicz et al) Reproducible technique for fabrication of thin films of high transition temperature superconductor's (See pages 1753-1755).	34-36

Form PCT/ISA/210 (extra sheet) (May 1988)